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SAFETY DESIGN CONSIDERATIONS FOR LITHIUM BATTERIES IN CF APPLIC--ETC(U)

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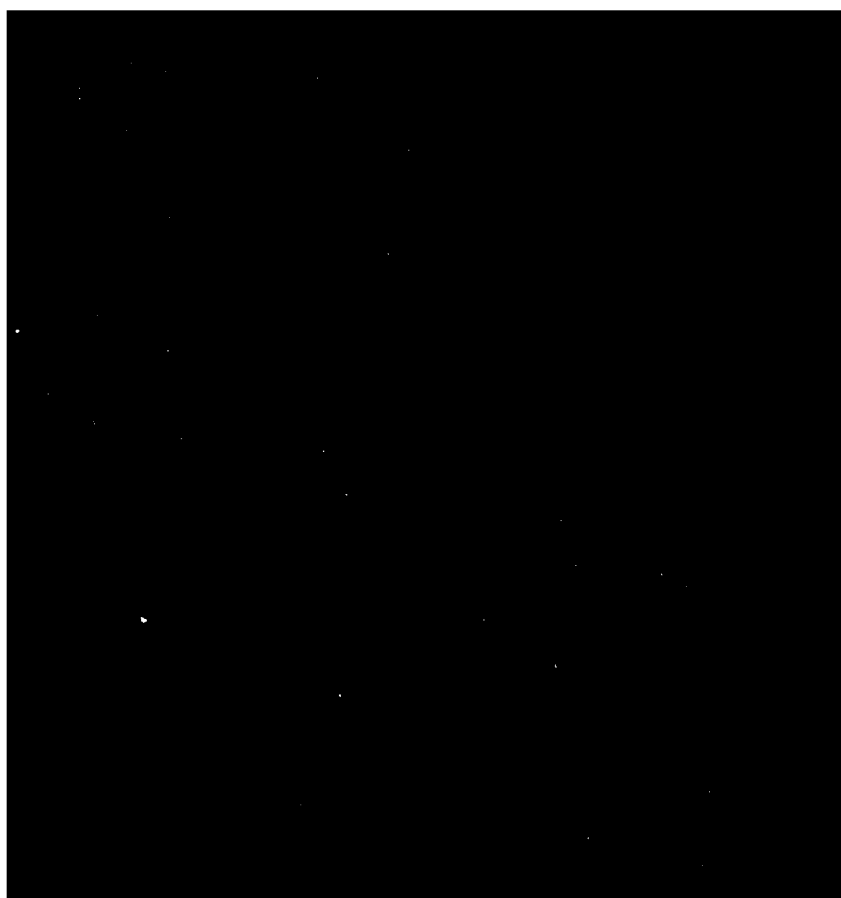
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**SAFETY DESIGN CONSIDERATIONS FOR LITHIUM BATTERIES
IN CF APPLICATIONS ***

by
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Chemical Sources Section
Energy Conversion Division

*NOTE: This paper was originally presented at the 11th meeting of the DND Director's Committee on Research Requirements and Development, held at DREO in September 1980.

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ABSTRACT

Résumé

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INTRODUCTION

Lithium-sulphur dioxide (Li-SO_2) primary cells are being introduced into CF applications where advantage can be taken of their high energy density characteristics and low temperature capabilities. Light, compact high power battery designs are now available for many military electronic applications such as sonobuoys, man-packed radios, radar transponders, and beacons.

For safety reasons, the high energy capabilities of these cells must be protected against the possibility of accidental abuse. DREO studies have aimed at investigating and identifying operational problem areas and where possible to propose remedial measures and safeguards.

This report will present some general background information on various lithium systems, examine the specific advantages and liabilities associated with Li-SO_2 batteries and discuss essential safeguards related to their use. Safety design considerations for Li-SO_2 batteries are proposed for three CF applications; the PRC 515 Radio²Set/Radar Transponder SST-181X applications, and the AN/PRQ-501 Personal Locator Beacon.

CHARACTERISTICS OF LITHIUM SYSTEMS

There are a number of lithium systems which are commercially available today. The more advanced of these systems are listed in the Table shown below. Of particular interest for CF applications are those having at least moderate rate capabilities (i.e. can deliver rated capacity at a 0.5 amp. rate in a D-size cell) and good low temperature (-40°C) performance. At the present time, very few lithium systems have these combined attributes and of these, only the Li-SO_2 is commercially available in mass production quantities. The bromine-complexed lithium cells (mfd. by Electrochem Ind. Inc.) and the moderate rate lithium-thionyl-chloride cells (wafer-type, mfd. by Altus Corp.) also listed in the Table are in the early production stages and should be available on the commercial market scene in 1981.

Advanced Primary Lithium Systems	
Low Rate	Moderate Rate
Carbon Monofluoride Thionyl Chloride Copper Oxide Silver Chromate Iodine Vanadium Pentoxide Manganese Dioxide	Sulphur Dioxide Thionyl Chloride Bromine-complexed

Certain electrical characteristics such as high energy density, and high cell voltages are common to all lithium systems. There are, however, some notable differences. The differences become apparent in current rate capabilities, low temperature performance, and system stability. Low rate cells are largely non-hazardous (operationally speaking), very stable, have low discharge rate capabilities in the microampere to milliampere range, and are relatively poor in low temperature performance. The moderate rate cells on the other hand, have better discharge rate capabilities in the milliampere to ampere range, good low temperature performance, and generally have more reactive and in some cases less stable constituents. Low rate cells make excellent batteries for heart pacemakers, calculator and wrist-watch applications. Moderate rate cells are better suited to meet the needs of power supplies for more demanding electronic applications.

The energy density output of the Li-SO_2 system is considerably superior to other conventional primary systems when compared at moderate rates of discharge; at C/20 to C/10 rates. The extent of this superiority over the operational temperature range of -40° to $+60^\circ\text{C}$ is shown in Figure 1 (Ref. 1). At these rates of discharge, present day low-rate thionyl chloride cells lie approximately midway between conventional and Li-SO_2 cells in energy density output. According to their manufacturers (Ref. 2 and 3), the energy density output curves of new thionyl chloride and bromine complexed cells are expected to compare favourably with that of Li-SO_2 .

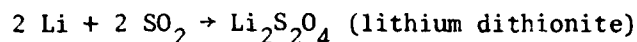
LITHIUM SULPHUR DIOXIDE CELL CONSTRUCTION

The basic construction of a Li-SO_2 cell is not unlike that of a conventional cell and contains the same essential components; ie. a positive electrode, negative electrode, separator, and electrolyte. The constituents of the principal components are, however, unique to the Li-SO_2 system. The positive electrode consists of porous carbon with sulphur dioxide (SO_2) as the chemically active material. The negative electrode is metallic lithium foil. The separator material is microporous polypropylene. The electrolyte is a solution of lithium bromide in acetonitrile which is a non-aqueous organic solvent.

A cut-away drawing illustrating the wound anode construction that is used in Li-SO_2 cells is shown in Figure 2 (Ref. 4). The wound anode or "jelly roll" construction is achieved by spirally winding sequentially layered rectangular strips of lithium foil, separator material, carbon cathode, and more separator material into a cylindrical configuration which is inserted into the metal cell container. Sulphur dioxide, together with the electrolyte is added to the cell in the latter stages of cell construction.

Distinctive features of the Li-SO_2 cell construction are (1) a high internal pressure of 3-4 atmospheres that is required to keep the SO_2 liquefied at normal temperatures, (2) a safety vent mechanism to preclude cell rupture or explosion in the event of inadvertent cell abuse, (3) a glass-metal seal to isolate the positive electrode from the negative cell container, and (4) a hermetically sealed (welded) container.

The energy producing chemical reaction in the Li-SO₂ cell can be written as:



During discharge SO₂ is reduced at the carbon cathode and combines with lithium ions to produce the reaction product lithium dithionite. In general the capacity of a cell is dependent on the quantity of reactants that are internally available. The energy producing reaction normally continues until the supply of reactants is depleted. In the conventional Li-SO₂ cell design, SO₂ is the capacity limiting reactant and lithium is available in excess.

PROBLEMS AND HAZARDS

The degree of violence with which an electrochemical system responds to abuse is in great measure directly proportional to its energy content or energy density, and the rate or ease with which this energy can be withdrawn. The high energy density of the Li-SO₂ system which is 2 to 5 times greater than what is available from the well known conventional systems, and its capability for high rates makes this system exceptionally hazardous if subjected to abuse conditions.

Two failure modes are possible. The cell rapidly vents its pressurized contents as intended by design, i.e. a quiet venting occurs which is comparable to the effect achieved by opening the tab on a soft drink beverage can, or the cell vents violently with much heat, flame, fumes and smoke. In both instances, noxious fumes are released which can cause corrosion to electronic equipment and severe discomfort or even incapacitation to personnel. The latter case of violent venting also introduces the serious possibility of a fire hazard.

CONDITIONS LEADING TO ABUSE POSSIBILITIES

The conditions that can lead to abuse possibilities with hazardous consequences can be either electrical or physical in nature. Electrical abuse conditions can include short-circuits, re-charging and forced over-discharge while physical abuse can include such conditions as mutilation, incineration, high temperature storage, and even encapsulation.

While the effects of physical abuse such as mutilation and incineration have a high visibility profile because they result in an immediate and obvious release of energy, the harmful effects of storage at elevated temperatures (71°C) are insidious and slow. DREO has found such storage to be the cause of progressive cell deterioration that can result in capacity loss and ultimate cell failure. The rate of corrosive attack upon glass/metal seals (Ref. 5) and electrode tab connectors by the hostile chemical environment within a cell is greatly increased by high temperatures. Non-destructive X-ray techniques used at DREO have proven to be a useful

analytical tool for making in-situ observations on cells subjected to high temperature storage.

Electrical abuse conditions that can lead to the development of hazardous situations are short circuits, re-charging, or forced over-discharging. Short circuit conditions generally result in cell ventings but re-charging or forced over-discharging can result in explosions or violent ventings of a more hazardous nature. Hard encapsulation can aggravate an already serious abuse condition by hindering or preventing the vents from functioning in their normal manner.

Abuse conditions involving short-circuits and re-charging can be prevented through the judicious use of fuses and diodes. The control of forced over-discharge in conventional cells is a more difficult problem for which various preventative measures are presently being investigated.

FORCED OVER-DISCHARGE

A forced over-discharge condition can result in a violent venting or even an explosion. Evidence indicates that the hazardous nature of this condition originates in the spontaneous reaction of unused lithium with acetonitrile electrolyte in the absence of SO_2 depolarizer which has been consumed during the cell discharge reaction (Ref. 6). Circumstances leading to such a situation are most likely to develop in the cell of a battery which for some reason has prematurely lost or discharged a significant portion of its rated ampere hour capacity, and then is over-discharged into a reverse polarity condition by other series connected cells during an ensuing power drain.

Causes of premature capacity loss in a cell can include leaking seals, internal short circuit mechanisms and poor battery circuit designs that incorporate disproportionate cell loading. Although statistics involving incidents of forced over-discharge have been difficult to establish, events of this type involving considerable battery damage have been known to occur (Ref. 7). The nature of failure mechanisms leading to forced over-discharge problems are such, that to-date preventative measures based on external controls have been difficult to effect. The most promising control measures appear to lie in the direction of internal improvements to the cell design, namely in the areas of better glass-metal seals and by the elimination of excess lithium through electrochemically balanced cells.

A typical voltage and temperature profile of a D-sized Li-SO_2 cell that was deliberately driven into a forced over-discharge condition and into violent venting at -40°C is shown in Figure 3. The interesting points to note are the low value of current (0.25 Amp) under which this condition was achieved, and the extremely low cell temperature (-8°C) registered by the cell just prior to venting. This clearly shows that where a cold environment is encountered, hazardous reversal conditions can occur at very ordinary current rates that are commonly used in many portable electronic applications. It also reveals that the reaction is extremely rapid and unstable even in the absence of heat, and that heat per se is not

a reaction prerequisite but really an external manifestation of the reaction process.

DESIGN CONSIDERATIONS

There are a number of options available to the battery designer by which electrical abuse hazards can be minimized in Li-SO₂ battery applications although it is doubtful that they can be totally eliminated. Acceptably safe designs can be achieved through the implementation of some or all of the following safeguards:

Balanced cells manufactured with a 1:1 coulometric ratio of lithium to sulphur dioxide have eliminated the unstable presence of excess lithium in over-discharge circumstances. However, at the present time balanced cells are available in D-sizes only. Market considerations will dictate the eventual availability of other sizes.

Fusing at the lowest amperage rating that is practicable for the application in question is recommended in order to prevent discharge at higher than specified rates.

Diodes must be used between parallel strings of Li-SO₂ cells in a battery as protection against charging. However, paralleling of cells should be avoided if more appropriate cell sizes are available. The use of diodes as individual protective devices for cells against forced over-discharge is also being investigated.

Thermal fusing protection is recommended in applications where extended high current drains and/or cell heating due to high environmental temperatures above 100°C is a possibility.

Matched duty cycles must be maintained for all cells within a battery in order to avoid unbalanced loading on a battery section that can lead to forced over-discharge conditions.

A design problem presently frustrating the attainment of a safe long-lived Li-SO₂ battery has been the unpredictable longevity of the glass-metal seals under prolonged ambient storage conditions. At the present time, two years appears attainable but lifetime predictions beyond this period are uncertain due to an insufficient data base. As mentioned previously, leaking and corroding seals can lead to premature capacity loss and forced over-discharge possibilities. Until all seal problems are satisfactorily resolved, it is advisable that periodic inspections of battery cells be carried out in order that leakage problems if present can be detected in their incipient stages and that problem batteries can be removed from service immediately.

Within the total package design it is strongly recommended that the battery compartment be physically separated and isolated from the electrical circuitry in order to protect the components from corrosion damage if an SO₂ leak or a venting should occur. The battery compartment should be

capable of containing these emissions or be designed to vent them safely to the exterior.

Within the compartment itself, hard encapsulation of battery cells should definitely not be considered because it can prevent cell vents from functioning in their normal manner with rather disastrous consequences. With reservations, soft encapsulation may be used provided it does not interfere with the normal functioning of the cell venting mechanism. However obvious disadvantages associated with the use of soft encapsulation are that it acts as a heat insulator and thus aggravates heat related problems, and secondly that by obscuring the cell pack it virtually eliminates the possible detection of cell defects by visual means.

DUAL PURPOSE LITHIUM BATTERY

The PRC 515 Radio Set and the Radar Transponder SST-181X are two distinct and separate applications whose power requirements are sufficiently similar to warrant the consideration of a single Li-SO₂ battery design for their power supplies. In 1979 a development contract was arranged with the Mallory Battery Co. of Canada Ltd. under the task sponsorship of the Directorate of Land Armament and Electronic Engineering and Maintenance (DLAEM), and with DREO as the scientific authority, to produce a Li-SO₂ battery design capable of meeting the dual specifications. Scheduled completion date for the contract is September 1981.

The PRC 515 Radio Set is powered by a rechargeable nickel cadmium battery (BB 706U), while the Radar Transponder uses a primary zinc alkaline battery (BA 3515A). In order to better meet operational needs, alternative primary battery systems are being sought for both applications. In the one case, DND equipment policy requires that a viable primary battery alternative to rechargeable batteries be available for man-packed radio sets, while in the other, the primary zinc alkaline battery which was originally designed for another application cannot adequately meet all the cold weather requirements. The specifications for the dual purpose battery are shown in the Table.

General Specifications

Operational Requirements	PRC 515 Radio Set	Radar Transponder SSt-181X
Voltage	24-31 volts	Same
Current	1A:0.06A on 1:9 duty cycle	0.7A
Output	30 watts	18 watts
Service life	12 hrs. at 25°C	6 hrs. at 25°C 3 hrs. at -40°C
Weight	<2.3 kg (5 lb.)	Same

The various design features of the new dual purpose Li-SO₂ battery are listed below:

- . Separate battery compartment
- . Coulometrically balanced D-size cells
- . Two strings of eleven cells in parallel
- . Diode protection between strings
- . Diode protection of individual cells (under investigation)
- . Fuse protection; 6 amp. rating to meet PRC 515 antennae tuning requirement of 4 amp. for 7 sec.
- . Battery weight of approximately 4 lb. (1.8 kg).

The concept of diode protection for individual cells against the danger of forced over-discharge is presently under investigation. The diode, acting as by-pass device would prevent the voltage of a cell from being driven to a dangerous negative value. This hazardous reversal value has been found to be approximately -0.75 volts. Diodes suitable for this purpose are being investigated.

High amperage fuse ratings in these applications are naturally a matter of some concern, since prolonged high current discharges in conjunction with Li-SO₂ cells are a recognized hazardous combination. In this case, protection against this potential hazard is provided by a time-delay switch in the tuning circuit which effectively limits the tuning operation to seven seconds, followed by an automatic fifteen second shut-down period until the set is tuned. A prolonged high current discharge possibility is thereby avoided.

If the development phase is successful, the dual purpose battery designed for the PRC 515 Radio Set and the Radar Transponder should have the capability to meet both the difficult operational requirements and the safety demands of these applications.

LITHIUM BATTERY FOR THE NEW CF PERSONAL BEACON

The new AN/PRQ-501 Personal Locator Beacon (PLB) shown in Figure 4, was designed by the Garrett Manufacturing Ltd. (Toronto) under a contractual arrangement with the Directorate of Avionics and Armament Subsystems Engineering (DAASE, now DAVSSE), to meet the PLB specifications stipulated in the Department of National Defence document, RAD 62-3. The principal operating requirements set out in this document are as follows:

- . Operating voltage: 8-11 volts
- . Load current: 25 mA in beacon mode; 50 mA in voice mode

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- Power output: 325 mW minimum
- Operational capability: 24 hrs. from -40°C to $+55^{\circ}\text{C}$
- Total PLB unit weight: 2 lb. (908 grams)
- Total PLB unit size: 6.75 in x 3.1 in x 1.5 in
(17 cm x 7.9 cm x 3.8 cm)

The small hand-held electronic unit with two way voice capability weighs about 1.3 pounds exclusive of battery. Weight allowance for the battery is about 0.7 lbs. The battery is designed to be contained in a physically separate slide-in compartment which locks into position on the bottom of the electronic unit. The ultimate size of the battery compartment will, of course, depend on the type of cells selected for the power supply, but with a high energy density battery system it is not expected to exceed much more than one-third of the overall unit length. A high energy density system having good low temperature performance is needed to meet the electrical performance requirements within the desired weight and volume restrictions. The most promising battery system that is presently commercially available to meet the demands of this application is the Li-SO_2 system.

Pending the procurement of suitable Li-SO_2 batteries, lithium-carbon monofluoride cells have been tried as an interim power supply for the PRQ-501. However, despite the high energy density of this system, its low temperature performance left much to be desired and severely restricted the winter capability of the PLB. It, therefore, became highly desirable that a qualified battery system be obtained for this application as quickly as possible. An assessment of the performance of aged lithium-carbon monofluoride cells in the PLB application was conducted by DREO in March 1980 (Ref. 8).

The principal safety features to be incorporated in the proposed Li-SO_2 battery for the PLB application are listed below:

- Separate battery compartment
- Coulometrically balanced cells (if available)
- 4 C-size cells in series
- Diode protection of individual cells (under investigation)
- Fuse protection 0.1 Amp

An intrinsic operational condition which makes an important contribution towards reducing the risk factor in this application is the low power requirement of the PLB unit. Consequently, only a small number of cells are needed for the battery and this feature together with the low current demand combine to reduce the number of individual elements that can contribute to the hazard potential.

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The performance of a four cell Li-SO₂ battery, comprised of C-size cells, in the new PLB application is shown in Figure 5 (Ref. 9). As can be seen from the curve, the performance of the battery pack far exceeds the minimum specified requirements which are designated by the dotted lines. The battery delivered more than 90 hours of operation over the complete temperature range of -40° to +55°C.

Evaluation trials of the complete battery and PLB units scheduled by DAVSSE for 1981 should provide answers as to the ability of the battery design to meet the desired performance and safety standards.

CONCLUSIONS

There is an ever growing demand in the military for light, compact, high power battery designs for electronic applications. At the present time, the Li-SO₂ battery system is the only one which is commercially available that combines both the high energy density and low temperature capabilities which are needed to meet the demands imposed upon equipment by the severe climatic conditions to be found in Canada during the winter-time.

However, a serious disadvantage of the Li-SO₂ system is its natural inclination to react violently under various abuse conditions. Therefore, safeguards must be incorporated into the battery design to protect the equipment user. The hazards can be minimized to an acceptable risk level, but there is no guarantee that they can be totally eliminated.

Two Li-SO₂ battery designs complete with safeguards have been proposed by DREO for use by the Canadian Forces. The batteries are to be used in the PRC 515 Radio Set/Radar Transponder SST 181-X and PRQ-501 Personal Locator Beacon applications. These batteries should be available for evaluation trials in 1981.

There are several promising, new lithium systems emerging in the commercial market that could provide serious future competition to the Li-SO₂ system in terms of energy density and low temperature capability. Of major significance are the claims that these new battery systems are inherently safe when subjected to abuse conditions and therefore, do not require the extensive safety precautions that presently must be incorporated into Li-SO₂ battery designs.

The new systems of interest are the lithium-halogen complexed cells (mfd. by Electrochem Industries, U.S.A.) and the wafer type lithium-thionyl chloride cells (mfd. by Altus Corp's, U.S.A., and possibly others). There is little doubt that if their performance potential is realized, then these new systems will be preferred to Li-SO₂ and that they will find extensive use in both military and civilian applications.

In the meantime the advantages of the Li-SO₂ electrochemical system can be fully utilized in military electronic applications provided the shortcomings of this system are duly recognized and that appropriate

measures are instituted to protect the system against the possibility of accidental abuse.

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4. AN/PRQ-501 Personal Locator Beacon.
5. Performance of a Li-SO₂ battery in the PLB application.

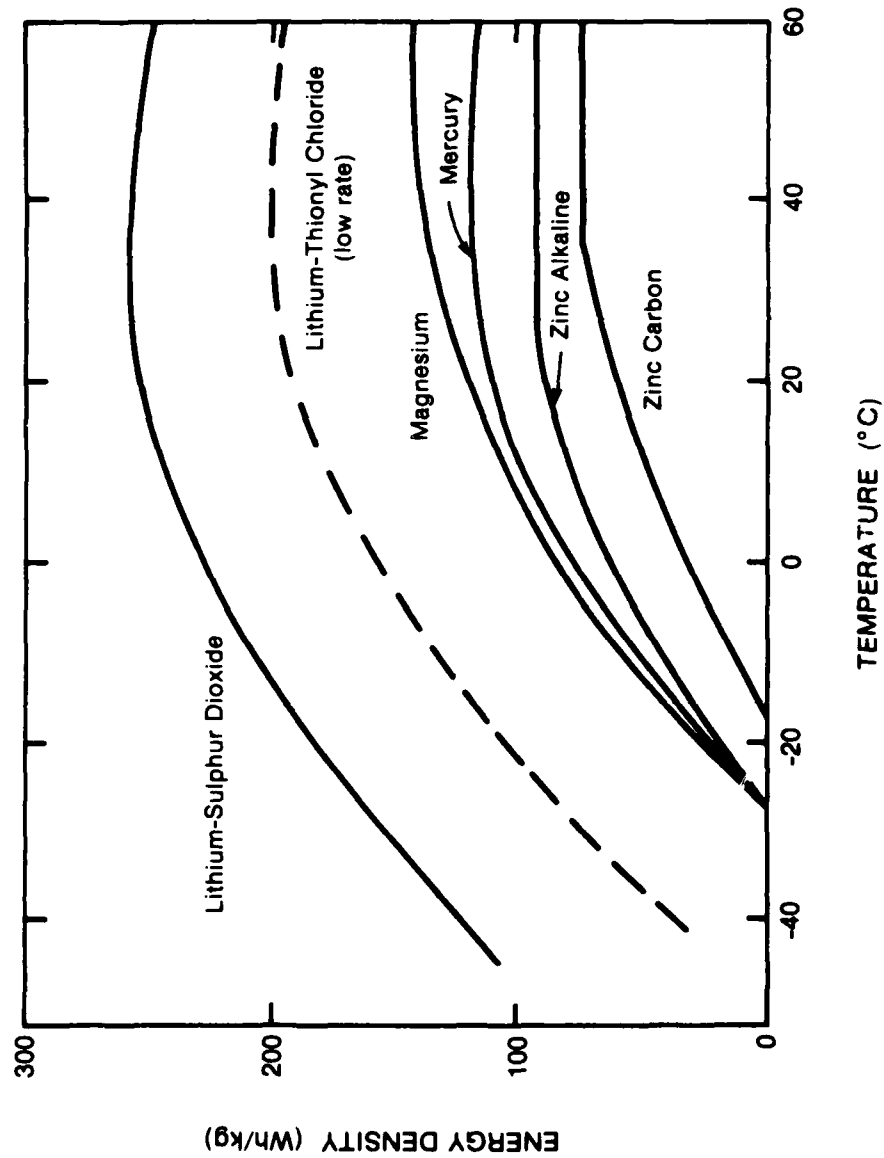


Fig. 1: Comparative performance of various primary battery systems at moderate rates (C/20 to C/10).

LITHIUM - SULPHUR DIOXIDE CELLPRINCIPAL COMPONENTS

Negative Electrode : Lithium Foil
Positive Electrode : Carbon/Sulphur Dioxide Depolarizer
Separator : Microporous Polypropylene
Electrolyte : Acetonitrile + Lithium Bromide Salt

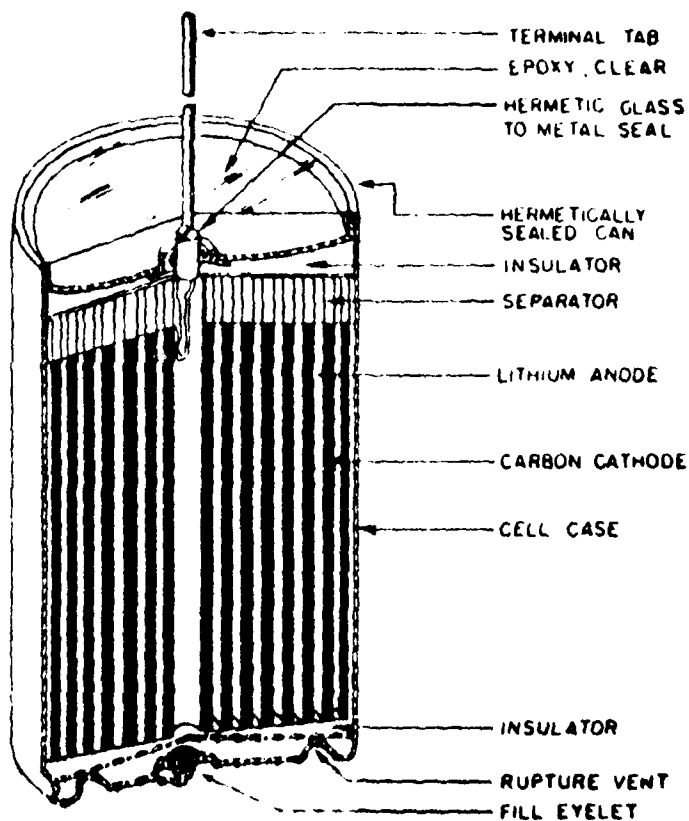


Fig. 2: Sectionalized view of Li-SO₂ cell construction.

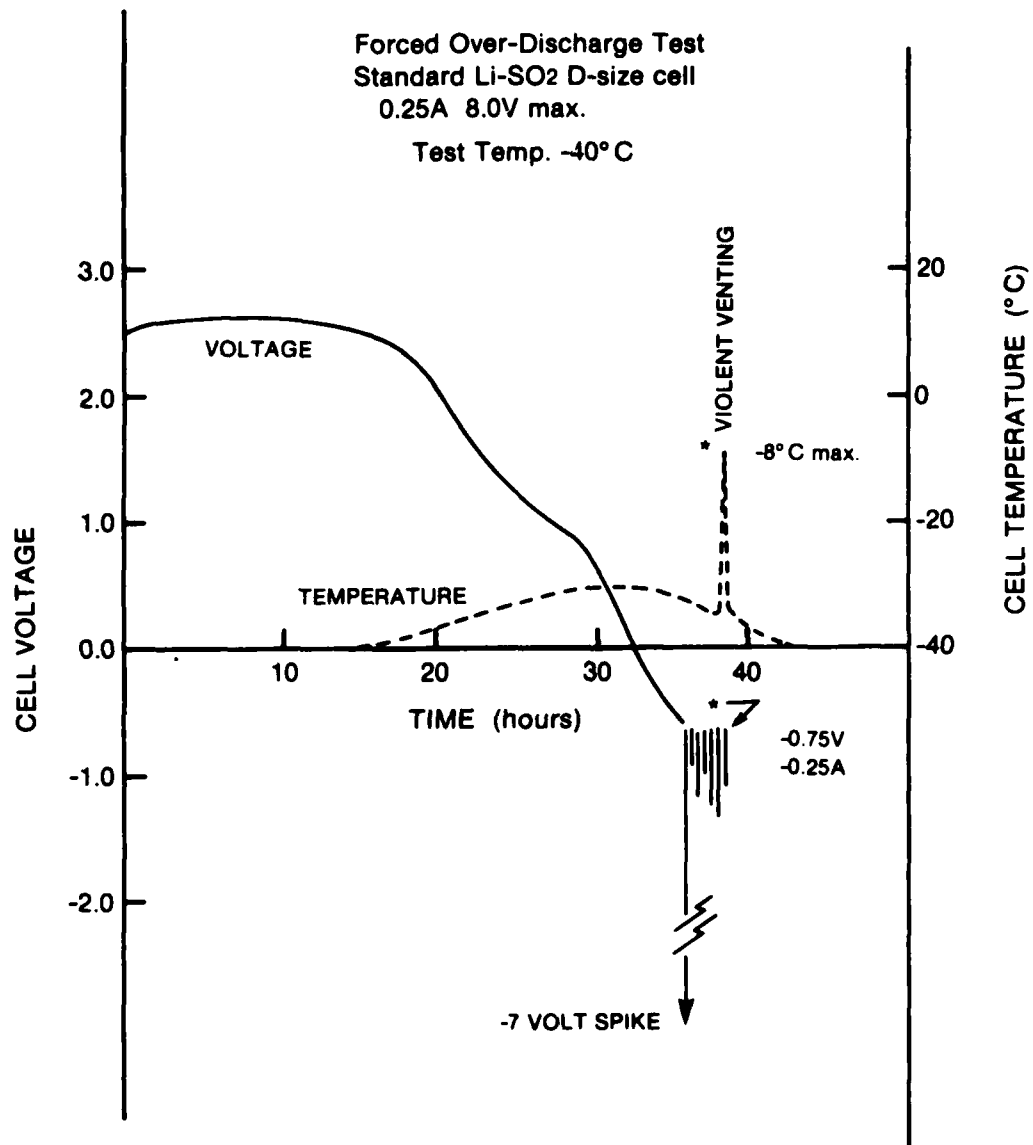


Fig. 3: Typical voltage and temperature profile of a Li-SO₂ D-size cell in a forced over-discharge condition at -40° C.

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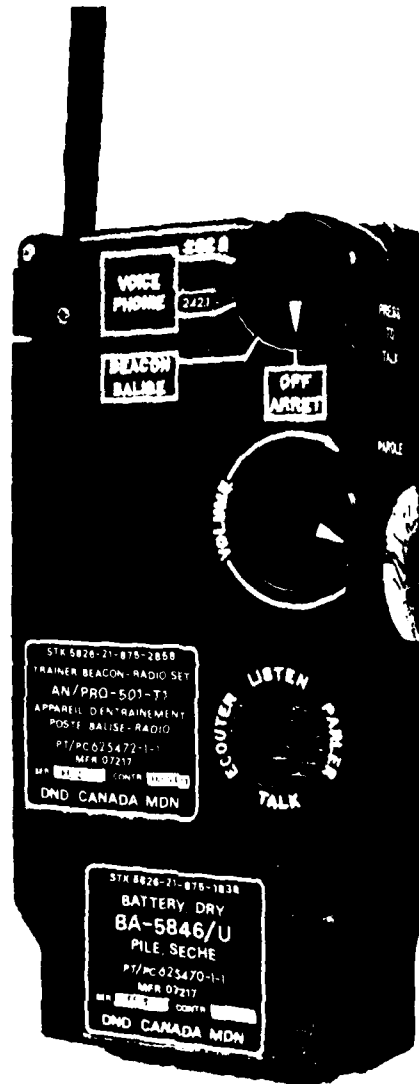


Fig. 4: AN/PRQ-501 Personal Locator Beacon

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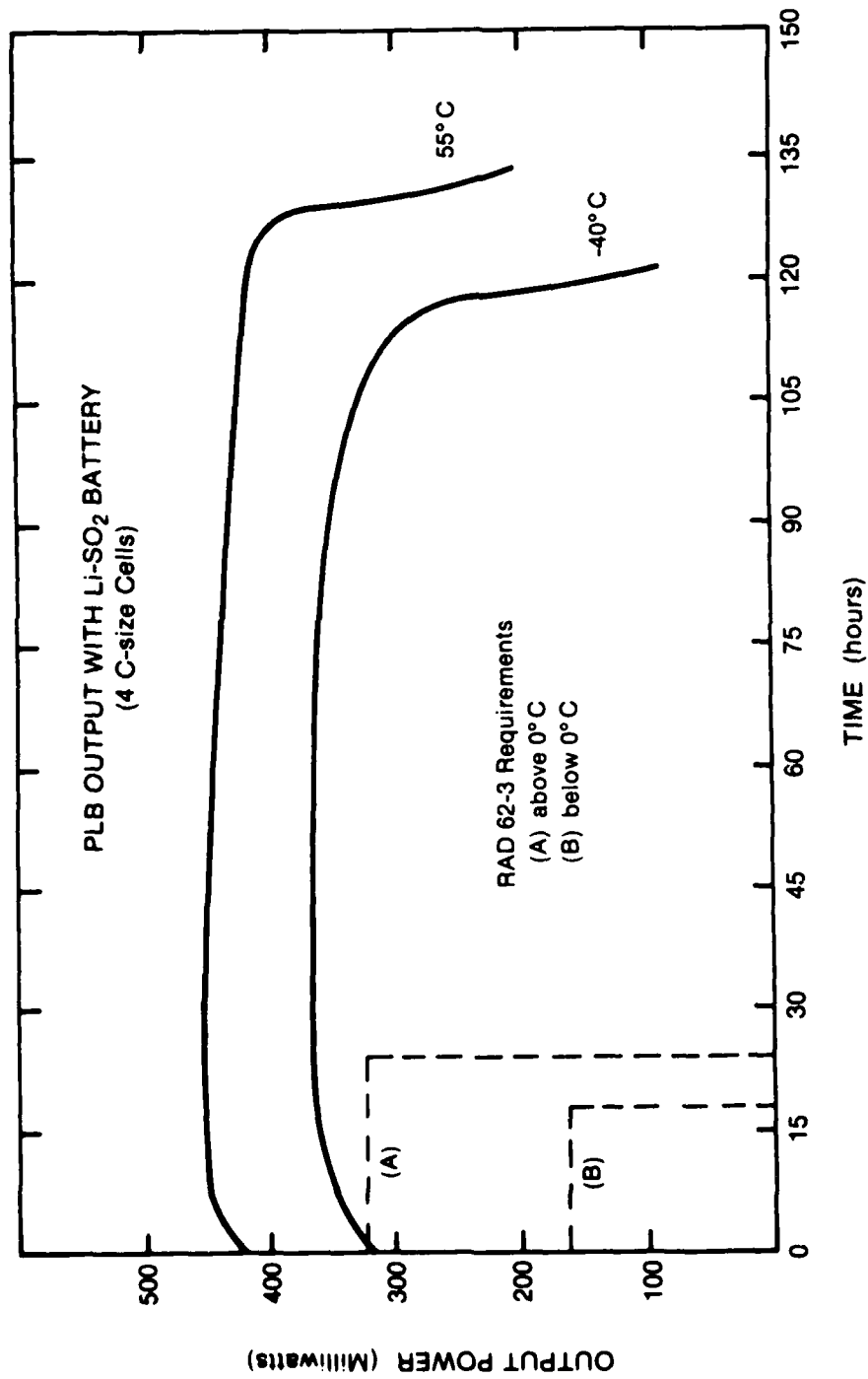


Fig. 5: Performance of a Li-SO₂ battery in the PLB application

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lithium-sulphur dioxide batteries,
lithium battery abuse,
lithium battery safety considerations,
lithium batteries for CF applications

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